

APPENDIX A

SENSITIVITY ANALYSIS, SOURCE TERM REFINEMENT, AND ENVIRONMENTAL MONITORING DATA FOR CARBON TETRACHLORIDE

ROCKY FLATS DOSE RECONSTRUCTION PROJECT
Technical Memorandum OCT15-CDPHE-RFP-1997**SENSITIVITY ANALYSIS, SOURCE TERM REFINEMENT, AND ENVIRONMENTAL
MONITORING DATA FOR CARBON TETRACHLORIDE**

prepared by
Arthur S. Rood
K-Spar Inc., Rigby, Idaho 83442
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Radiological Assessments Corporation

INTRODUCTION

Estimated carcinogenic risks from the inhalation of carbon tetrachloride released from the Rocky Flats Plant (RFP) are documented in [McGavran and Rood](#) (1997) and results were presented at the May 1997 Health Advisory Panel meeting in Denver, Colorado. At this meeting, several requests were made for additional calculations and refinements to the estimated risks. Specifically, requests were made for a sensitivity analysis of the risk calculations for the rancher scenario, and a reevaluation of the assumptions underlying the source term estimates. In particular, a request was made to reexamine the assumption that 100% of the carbon tetrachloride used at the site was emitted to the atmosphere. This technical memorandum documents a sensitivity analysis for the rancher scenario and examines diffusion of carbon tetrachloride in the subsurface. Diffusion calculations are needed to evaluate the fraction of carbon tetrachloride emitted to the atmosphere from a ground surface disposal.

In addition to these items, recent inquiries into carbon tetrachloride monitoring at Rocky Flats has uncovered some ambient measurements performed in 1989 that were not reported in the Task 4 report. A summary of these data are presented.

SENSITIVITY ANALYSIS

The rancher exposure scenario is described in detail in [McGavran and Rood](#) (1997). The scenario places the receptor (the rancher) at the point of highest concentration outside the buffer zone and along Indiana Street ([Figure 1](#)). The scenario represents an upper bound estimate to risk and is hypothetical in nature. These risks are near the point of departure for acceptable risks defined by the U.S. Environmental Protection Agency (EPA). Acceptable risks are in the range of 10^{-6} to 10^{-4} . Because the risks are near the range of departure for acceptable risks, a sensitivity analysis was performed to determine what parameters have the greatest impact on the risk.

A sensitivity analysis is used to assess the sensitivity of a given computational endpoint (in our case, carcinogenic risk) to changes in parameter values that affect the endpoint. Each parameter is then ranked according to its contribution to the overall variance in the end

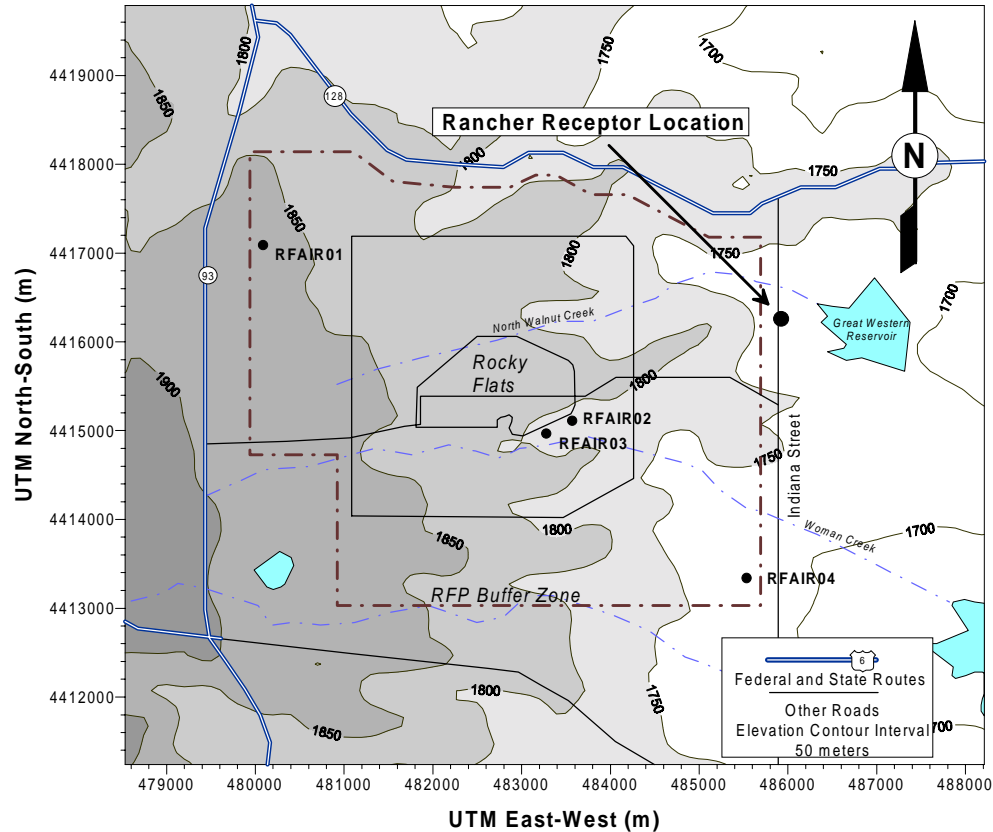


Figure 1. Map of Rocky Flats Plant showing location of the buffer zone, receptor location for the rancher, and location of air samplers.

point. The sensitivity a model parameter may have on the end point is a function of its mathematical importance and its expected range. For example, consider the equation

$$D = A^B + C \quad (1)$$

where A is a fixed value, B and C are stochastic, and A is much greater than (\gg) C . If B and C are distributed identically, B will likely be more sensitive than C because B is in the exponent in Equation (1). The opposite is true if $C \gg A$ and B is distributed within a narrow range.

Carcinogenic risk (R) for carbon tetrachloride inhalation by the rancher was calculated using the equation

$$R = \frac{TIC SF (BR_1 T_1 + BR_2 T_2 + BR_3 T_3)}{BW AT} \quad (2)$$

where

- TIC = time-integrated concentration (stochastic),
- SF = slope factor for carbon tetrachloride (stochastic kg d mg^{-1}),
- BW = body weight (78.7 kg),
- AT = averaging time (25,550 days),
- $BR_{1, 2, 3}$ = breathing rate for occupational, nonoccupational, and sleeping respectively,
- $T_{1, 2, 3}$ = hours spent in occupational, nonoccupational, and sleeping activities respectively.

The time-integrated concentration is given by Equation (3)

$$TIC = CF_1 \sum_{i=1}^n CF_2 CF_3 \sum_{j=1}^m \frac{\chi_j}{Q} Q_{i,j} \Delta t \quad (3)$$

- χ/Q_j = dispersion factor for source j ($y \text{ m}^{-3}$),
 $Q_{i,j}$ = source term for year i and source j (stochastic, mg y^{-1}),
 CF_1 = stochastic correction factor for dispersion (unitless),
 CF_2 = stochastic correction factor meteorology (unitless),
 CF_3 = stochastic correction factor for deposition (unitless),
 n = number of years exposed,
 m = number of sources,
 Δt = time increment (1 year).

The stochastic variables in Equation (2) and (3) are all independent and monotonic. That is, an increase in an assumption (stochastic variable) is accompanied by increase in the target forecast (risk), or and increase in a stochastic variable is accompanied by decrease in the target forecast. The terms in the summation symbol represent the integrated concentration over the exposure period and number of sources. Note that dispersion correction factor is outside the summation symbol in Equation (3). The correction factor applies to any long-term average concentration (> 1 year) regardless of the integration time and is sampled once for each Monte Carlo trial. The meteorology and deposition correction factors apply to each year the concentration is integrated over. These factors along with Q are sampled n times for each Monte Carlo trial.

The sensitivity analysis was performed using Crystal Ball software ([Decisioneering 1996](#)). Crystal Ball calculates sensitivity by comparing rank correlation coefficients between every assumption and every forecast cell while the simulation is running. Correlation coefficients provide a meaningful measure of the degree to which assumptions and forecasts change together. If an assumption and a forecast have a high correlation coefficient, it means that the assumption has a significant impact on the forecast (both through its uncertainty and model sensitivity). Positive coefficients indicate than an increase in the assumption is associated with an increase in the forecast. Negative coefficients imply the reverse situation. An output option allows the user to display the results in terms of the percent contribution to variance. The user is cautioned that this is only an approximation and is not precisely a variance decomposition. Crystal Ball calculates contributions to variance by squaring the rank correlation coefficients and normalizing them to 100%. For this reason, rank correlation coefficients and percent contribution to variance are both reported.

The stochastic variables defined above and their rank correlation coefficients and percentage contribution to the variance in carcinogenic risk are tabulated in [Table 1](#) and illustrated in [Figure 2](#). The dispersion correction factor accounts for most of the variability followed by the slope factor, source term, and meteorological correction factor for the 37-year exposure time. For the 1-year exposure time, the meteorological correction factor surpasses the slope factor in percent contribution to variance. This result is due to the different integration times. Longer integration time tends to reduce variability in the integrated air concentration estimate. These results may differ if the distribution of any one parameter is different than that used. One parameter of considerable importance was the slope factor. Distribution of the slope factor was taken from a preliminary estimate reported in [Weber](#)

(1997). This value was not expected to change appreciably from its initial estimate. Therefore, the overall conclusions of this sensitivity analysis are expected to remain valid.

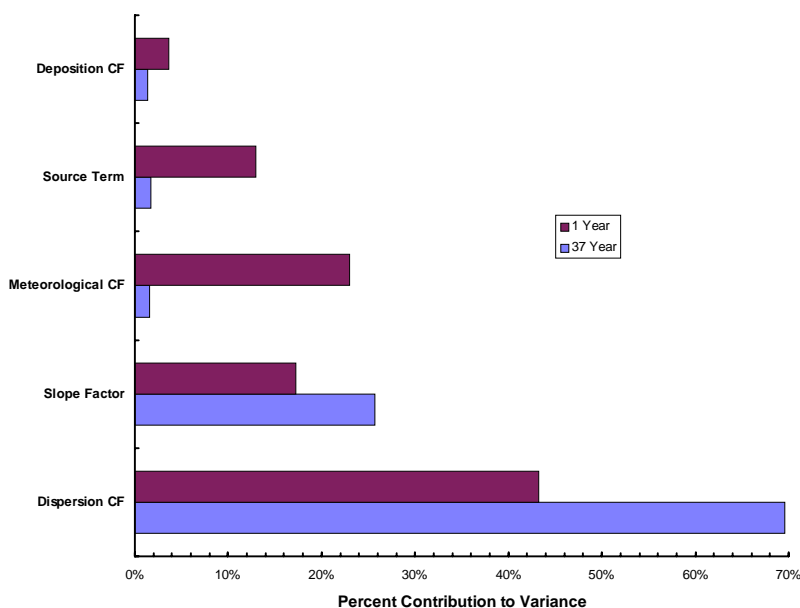


Figure 2. Percent contribution to variance in carbon tetrachloride risk estimates for the rancher scenario for a 37 and 1-year exposure time.

Table 1. Results of Sensitivity Analysis for Carcinogenic Risk using the Rancher Scenario and 1 and 37 Years of Exposure

| Parameter | Distribution Type ^b | 37-year exposure ^a | | 1-year exposure | |
|-----------------------------------|--------------------------------|-------------------------------|------------------------------|------------------|------------------------------|
| | | Rank correlation | Contribution to variance (%) | Rank correlation | Contribution to variance (%) |
| Dispersion correction factor | Lognormal 1.1 (2.2) | 0.83 | 69.6 | 0.66 | 43.2 |
| Meteorology correction factor | Lognormal 1.0 (1.7) | -0.03 - 0.03 | 1.6 | 0.48 | 23.0 |
| Plume depletion correction factor | Lognormal 1.0 (1.05) | -0.04 - 0.05 | 1.4 | 0.02 | 3.6 |
| Slope factor | Lognormal 0.025 (1.43) | 0.50 | 25.7 | 0.41 | 17.2 |
| Source term | Uniform 4–200 | -0.03 - 0.03 | 1.7 | 0.36 | 13.0 |

^a Correlation coefficients varied from year-to-year for the dispersion, meteorology, and plume depletion correction factors and release rate. The minimum and maximum rank correlation coefficients are shown in the table. The percent variance listed for each variable is the sum of all 37 years.

^b Statistics describing the distribution are listed below the distribution type. For lognormal distributions, the geometric mean (geometric standard deviation) are reported. For the uniform distribution the minimum–maximum value are reported.

RELEASE ESTIMATE REFINEMENT FOR GROUND SURFACE RELEASES

Release estimates for carbon tetrachloride assumed 100% of the inventory was released to the air. This assumption was made because carbon tetrachloride has a high vapor pressure and releases to soil or water would likely result in total evaporation in several hours to perhaps a few days. While it is understood that most of the carbon tetrachloride vapor will likely diffuse to the atmosphere, a fraction of it will remain in the subsurface. The fraction remaining in the subsurface is subject to diffusion (both upward and downward) and aqueous phase transport. Evidence of such phenomena has been observed at the Idaho National Engineering and Environmental Laboratory where carbon tetrachloride vapors in waste shipped from the RFP and disposed of at the Radioactive Waste Management Complex have been measured in the vadose zone and groundwater (Walton et al. 1989). In the calculations that follow, we attempt to estimate the downward flux of carbon tetrachloride and, thereby, estimate the fraction that is released to the atmosphere following a release to surface soil.

Consider the one-dimensional conceptual model illustrated in Figure 3. Carbon tetrachloride is released to the ground surface and moves downward in the liquid organic phase until the residual solvent saturation fraction (θ_r) is reached throughout the

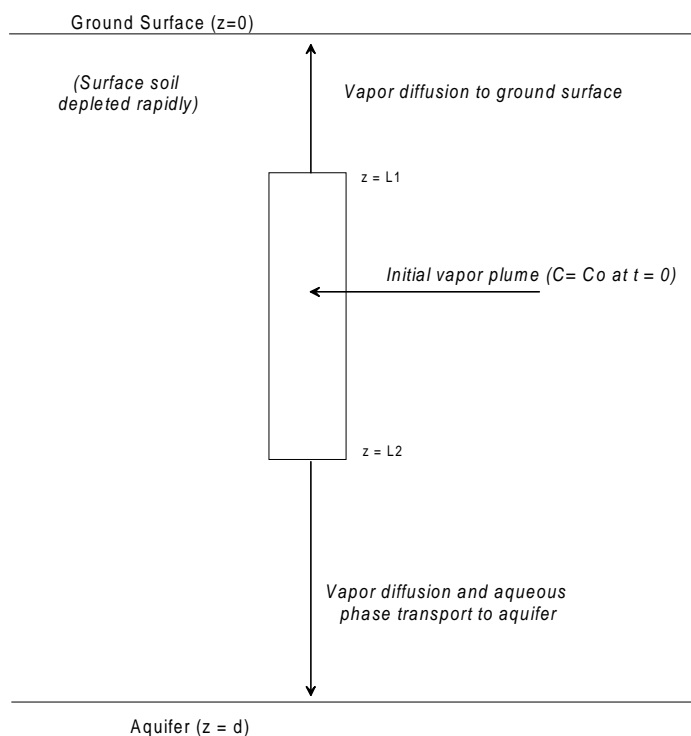


Figure 3. Conceptual model of carbon tetrachloride transport in the vadose zone following a release to the ground surface.

contaminated thickness of the soil column ($z = L1$ to $z = L2$). At the time when $\partial\theta_r/\partial z = 0$, the solvent is assumed to evaporate rapidly, and its vapor to occupy the air-filled pores in the porous media. The surface (10–20 cm in depth) is assumed to be depleted quickly, leaving a plume of carbon tetrachloride vapor in the vadose zone. A fraction of the vapor partitions into the pore water and the remainder diffuses in the gas phase. Assuming a constant diffusion coefficient in space and time, a steady-state water flux, and a homogeneous isotropic porous

medium, the mass balance equation for one-dimensional gas and aqueous phase transport in the subsurface is

$$\frac{\partial (\phi_a C_a + \phi_g C_g)}{\partial t} = \phi_g D_e \frac{\partial^2 C_g}{\partial z^2} - \frac{v \partial C_a}{\partial z} \quad (4)$$

where C_a = the concentration in aqueous phase (g cm^{-3}), C_g = the concentration in gas phase (g cm^{-3}), ϕ_a = aqueous-filled porosity, ϕ_g = gas-filled porosity, z is the depth below the surface (cm), v = the unsaturated Darcy velocity, and D_e = the effective diffusion coefficient in the porous media ($\text{cm}^2 \text{s}^{-1}$). Note that mechanical dispersion in the aqueous phase is ignored in [Equation \(3\)](#). The aqueous phase concentration is related to the gas concentration by the dimensionless Henry's law constant, H , and is given by $C_a = C_g/H$. Equation (4) can be rewritten substituting the previously stated relationship for C_a , and after some rearrangement it is written in terms of the gas-phase concentration as

$$\frac{\partial C_g}{\partial t} = \frac{\phi_g}{\phi_g + \phi_a / H} D_e \frac{\partial^2 C_g}{\partial z^2} - \frac{v}{H\phi_g + \phi_a} \frac{\partial C_g}{\partial z} \quad (5)$$

The direction of water flow is assumed to be on average, downward (into lower strata). It has been observed in cool arid climates, water flux to the subsurface tends to be negative during the summer months and positive in the spring where melting snow and cool temperatures allow water to infiltrate. ([Maheras et al. 1994](#)). Typically, there is an annual net water flux to the subsurface. Infiltration rates at the Idaho National Engineering Laboratory, which has a similar climate to Rocky Flats (perhaps a little drier), are around 2–7 cm y^{-1} and vary depending on the hydraulic properties of the unsaturated zone and annual precipitation.

Downward migration of carbon tetrachloride is assumed to continue until an aquifer is encountered. At that point, most of the carbon tetrachloride is dissolved in groundwater and transported away from the vapor plume in the unsaturated zone. At the surface, air movement above the ground surface removes most of the carbon tetrachloride at the air-soil interface. Given these assumptions, the following boundary conditions are applied to the model:

- $C_g = 0$, for $z = 0$ and $z = d$, for $t \geq 0$ (d = depth to aquifer)
- $C_g = C_o$ for $L_1 \leq z \leq L_2$ for $t = 0$ (see [Figure 3](#)).

The effective diffusion coefficient in soil can be estimated by ([Lyman et al. 1990](#))

$$D_e = D \left[\frac{\phi_g^{10/3}}{\phi_t^2} \right] \quad (6)$$

where ϕ_t = the total effective porosity and D = the diffusion coefficient in air ($\text{cm}^2 \text{s}^{-1}$). The diffusion coefficient in air can be estimated by ([Lyman et al. 1990](#))

$$D = \frac{10^{-3} T^{1.75} \sqrt{M_r}}{P(V_A^{1/3} + V_B^{1/3})^2} \quad (7)$$

where $M_r = (M_A + M_B)/(M_A M_B)$, M_A = molecular weight of air (28.97 g mol^{-1}), M_B = molecular weight of carbon tetrachloride ($153.84 \text{ g mol}^{-1}$), V_A = molar volume of air ($20.1 \text{ cm}^3 \text{mol}^{-1}$), V_B = molar volume of carbon tetrachloride ($94.5 \text{ cm}^3 \text{mol}^{-1}$), P = pressure (1 atm)

assumed), and T = temperature (K). The flux to the ground surface or aquifer is given by Equation 8.

$$F = -\phi_g D_e \frac{\partial C_g}{\partial x} + v C_g / H \quad (8)$$

Equations (5) and (8) were solved using an explicit finite difference technique described in [Press et al. \(1992\)](#). The cumulative flux was estimated by numerically integrating the flux from $t = 0$ to $t = t_e$, where t_e = the time where most of the mass has left the system. The ratio of the cumulative flux at the ground surface, to the total initial mass equals the fraction of carbon tetrachloride released to the air following a surface disposal.

Model inputs are listed in Table 2. The values are used only to demonstrate the model and will need to be refined if a more detailed estimate is required.

Table 2. Model Parameters for Carbon Tetrachloride Diffusion and Aqueous Phase Transport Model

| Model parameter | Value | Units |
|---------------------------------|----------------------|----------------------------------|
| Temperature | 15 | C |
| Diffusion coefficient in air | 0.077 | cm ² s ⁻¹ |
| Effective diffusion coefficient | 0.004 | cm ² s ⁻¹ |
| Finite difference grid spacing | 50 | cm |
| Total porosity | 0.3 | cm ³ cm ⁻³ |
| Air-filled porosity | 0.2 | cm ³ cm ⁻³ |
| Water-filled porosity | 0.1 | cm ³ cm ⁻³ |
| Unsaturated Darcy velocity | 3.2×10^{-7} | cm s ⁻¹ |
| Henry's law constant | 1.28 | dimensionless |
| Depth to water table | 2,000 | cm |

Initial gas phase concentrations were assigned to nodes at depths beginning at 50 cm and ending at 650 cm below the surface. Unit concentrations (1.0 g cm⁻³) were assigned to nodes 150 to 500 cm in depth. Concentrations of 0.25 g cm⁻³ were assigned to nodes at depths 50 and 600 cm and 0.5 g cm⁻³ for nodes 100 and 550 cm in depth.

The initial mass (M) in the system is given by

$$M = A \int_0^d \phi_g C_{go} + \frac{\phi_a}{H} C_{go} dz \quad (9)$$

where A = unit cross area (1 cm²), d = depth to the aquifer, and C_{go} = the initial gas phase concentration. Using the model parameters described in Table 2 and previously stated initial conditions, the total initial mass in the system was 134 g. Three-years following the release, 82 g were released to the surface, 4.8 g were released to the aquifer, and 45 g remained in the vadose zone. A mass balance error of about 3% was observed. These calculations indicate most carbon tetrachloride released to the ground surface is emitted to the atmosphere, but a fraction of it (probably 2-10%) remains in the vadose zone and ultimately ends up in groundwater.

ENVIRONMENTAL MEASUREMENTS OF CARBON TETRACHLORIDE

Additional investigation has discovered some limited measurements of carbon tetrachloride in air at RFP. These measurements were taken over a 3 day period in 1989 ([Lugar 1990](#)). Measurements were made on June 25, 28, and July 13, 1989. Samples were analyzed for 18 volatile organic compounds including carbon tetrachloride. Ambient air samples were collected at four sampling stations using the Tenax™ charcoal cartridges. Two sampling stations were located southeast of the plant security fence, one in the northwest corner near the buffer zone boundary, and one in the southeast corner of the buffer zone ([Figure 1](#)). Sampling was performed according to U.S. Environmental Protection Agency protocol IV-7, "Sampling for Volatile Organic Compounds" ([EPA 1984](#)). Samples were collected over an 8-hour period.

Carbon tetrachloride concentrations ranged from 0.2 to 2.0 $\mu\text{g m}^{-3}$ ([Table 3](#)). The day of highest concentration was July 13. The samplers near the plant security fence typically had the highest concentrations. The predominant wind direction during the sampling was from the northwest, but the wind direction was reported to be variable for the June 28 sampling period. Concentrations at the buffer zone were below the average background concentration of 1 $\mu\text{g m}^{-3}$ for carbon tetrachloride in the atmosphere ([Howard et al. 1991](#)).

Model validation using these measurements cannot be performed strictly quantitatively, because source term information for the days the measurements were made were not available and background levels were not measured on the day of sampling. Carbon tetrachloride was reported to have been used at Rocky Flats during the sampling period, but the quantities are unknown. However, a qualitative comparison can be made assuming a source term equivalent to the steady state release rate for 1989. RATCHET simulations were performed for the three sampling days and average concentrations were compared with the measured values. The uncertainty correction factor applied to the output was based on the distribution of 9-hr average predicted-to-observed ratios for RATCHET using the Winter Validation Tracer Study data ([Rood 1997](#)). The correction factor had a geometric mean of 1.2 and a geometric standard deviation of 4. Results of the simulations are illustrated in [Figure 4](#).

Predicted concentrations for June 25th exceeded the measured values for samplers at the security fence (RFPAIR02 and RFPAIR03) but underpredicted the concentration at sampler RFPAIR01. However, the measured concentration at that location was near the average background concentration for carbon tetrachloride (1 $\mu\text{g m}^{-3}$). Concentrations measured on June 28th were all below background and model predictions were less than these values. On that day, winds were light and variable resulting in no definite spatial pattern of carbon tetrachloride concentration in the area. Reasonably good agreement was found between predicted values and measured values for the July 13th sampling date. However, the buffer zone samplers (RFPAIR01 and RFPAIR04) had measured concentrations less than background.

These measured values illustrate a general decrease in concentration away from the plant except for day of June 28. Model predictions also show the same general pattern. This comparison suggests the models and source term used in the risk evaluation are not unreasonable. Annual average concentrations are typically lower. Predicted annual average carbon tetrachloride concentrations for 1989 at Indiana Street ([McGavran and Rood 1997](#)) ranged from about 0.2 to 4 $\mu\text{g m}^{-3}$.

Table 3. Measured Carbon Tetrachloride Concentrations in Air

| Date | Sampling station carbon tetrachloride concentration ($\mu\text{g m}^{-3}$) | | | |
|---------------|--|----------|----------|----------|
| | RFPAIR01 | RFPAIR02 | RFPAIR03 | RFPAIR04 |
| June 25, 1989 | 0.45 | 1.1 | 1.5 | 0.47 |
| June 28, 1989 | 0.39 | 0.42 | 0.34 | 0.41 |
| July 13, 1989 | 0.25 | 0.74 | 2.0 | 0.2 |

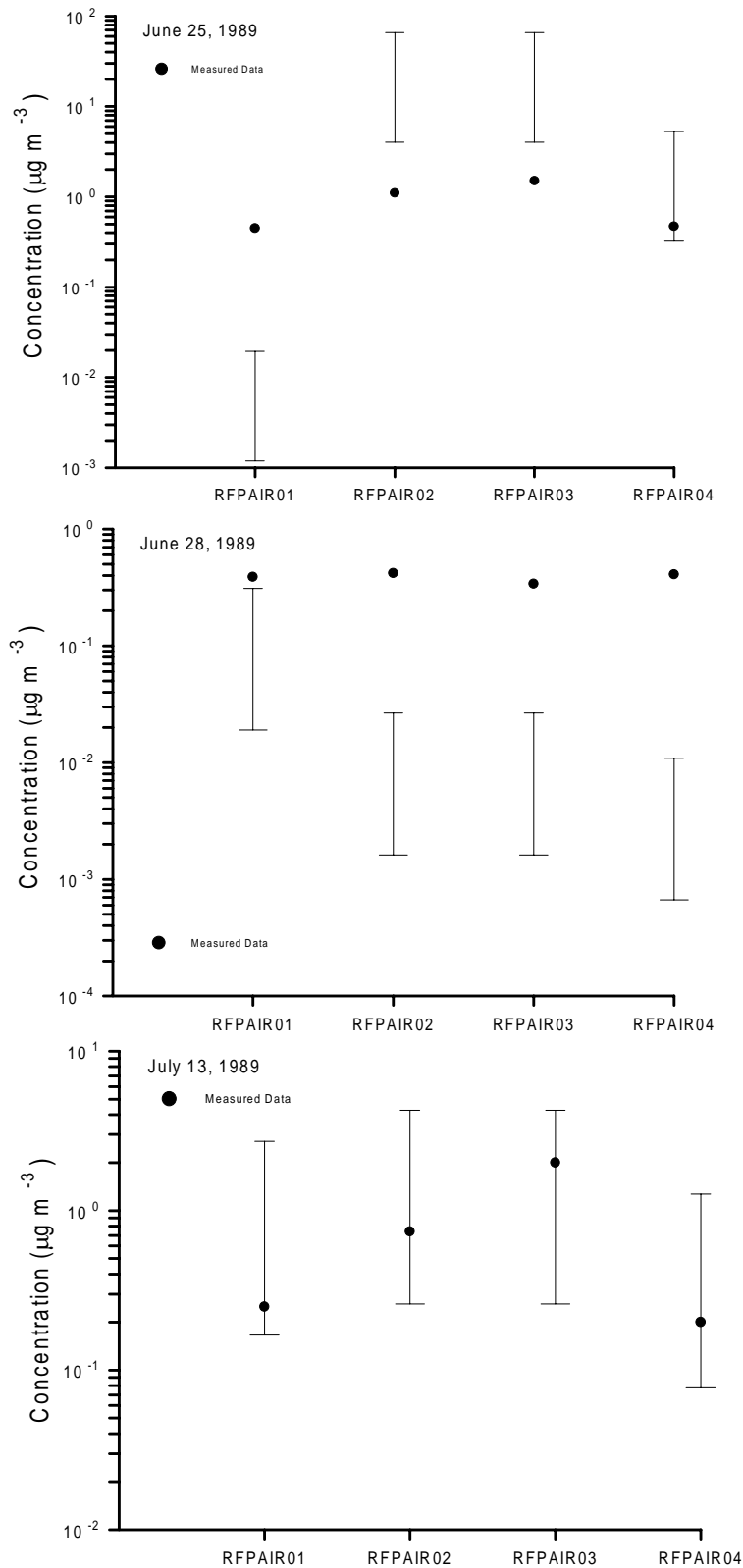


Figure 4. Predicted and measured carbon tetrachloride concentrations for three days in 1989. Error bars represent the 5th and 95th percentile values.

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